

Sorption of Octa(oxyethylene) Monododecyl Ether onto Silica Gel Studied by Liquid Chromatographic Methods^{†,‡}

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The adsorption of octa(oxyethylene) monododecyl ether (C₁₂E₈) from water onto silica gel—a system of technical as well as environmental interest—is investigated at various temperatures using liquid chromatographic techniques. The isotherms obtained are of the two-step type. The first step at low adsorbed amounts has scarcely been observed in the past. Therefore, this study focuses on this area. The sorption isotherms and the influence of temperature on these isotherms indicate different adsorption mechanisms for the two isotherm steps. Whereas the first step seems to be related to hydrogen bonds between hydrophilic surfactant groups and surface silanol groups, the second step can be well explained by the formation of hemimicelles on the surface. For the determination of the sorption isotherms, a liquid chromatographic technique, an elution analysis, is introduced. The so-called “elution on a plateau” technique measures the derivative of an isotherm and therefore can provide additional details about the course of the adsorption isotherm. In comparison with the common batch technique for the determination of sorption isotherms, the chromatographic method has several advantages. Temperature control of the measurement system is simpler. Furthermore, the investigation of the transport behavior and of poorly detectable substances such as poly(oxyethylene) monoalkyl ethers is possible.

Introduction

The adsorption of nonionic surfactants from aqueous solutions onto silica gel is of environmental as well as technical interest. Silica gel can easily be formed by silicic acid, which is a main inorganic component of soils and sediments. In general, silica gels possess high porosities and large surface areas. Therefore, artificial silica gels especially are often used technically as adsorbents or as carriers, e.g., for pesticides. Additional components of pesticide formulations are often surfactants as dispersing or wetting agents. Through agricultural applications of pesticides, formulation components such as surfactants can enter the soil. Furthermore, surfactants from detergents that have not been degraded can enter sewage and ultimately remain in the sediment or sludge, some of which is spread on fields. Nonionic surfactants are among the surfactants most frequently used. The most common nonionic surfactants are poly(oxyethylene) monoalkyl ethers and poly(oxyethylene) mono(alkylphenol) ethers. The contamination examples presented above illustrate why there is great practical interest in the adsorption of nonionic surfactants from aqueous solutions onto hydrophilic silica. This system is also of academic interest, so it has been intensively studied experimentally as well as theoretically.^{1–15} Furthermore, the influences of temperature,^{6,10,11} electrolyte,^{10,11} pH,¹¹ and lengths of the hy-

drophilic and hydrophobic groups^{8,10,11} on such adsorptions have been investigated. More recently, focus was directed toward the mechanisms and thermodynamics of formation as well as the structures of the adsorbed layers. Thus, modern experimental techniques such as X-ray diffraction,⁹ neutron reflection,⁵ atomic force microscopy,¹² calorimetry,^{6,7} photon correlation spectroscopy of silica sols,⁵ etc. have been employed.

For the determination of adsorption isotherms, the batch technique is often used. Sometimes chromatographic methods are utilized, e.g., frontal analysis in connection with flow microcalorimetry.^{6,7} Many systems such as soils or sediments are comparable to chromatographic columns. The transport processes in such systems can be simulated by liquid chromatography in contrast to the batch method.

In the present work adsorption isotherms are measured by a chromatographic technique related to frontal analysis, the “elution on a plateau” method,¹⁶ which has been scarcely used in liquid chromatography up to now. In contrast, in analytical elution chromatography, it is commonly desired to work only at the linear beginning of an isotherm. For the adsorption of poly(oxyethylene) monoethers from water onto silica, often only S-shaped isotherms are found,^{5,6,10} whereas there are only a few examples of two-step isotherms, i.e., Langmuir-type

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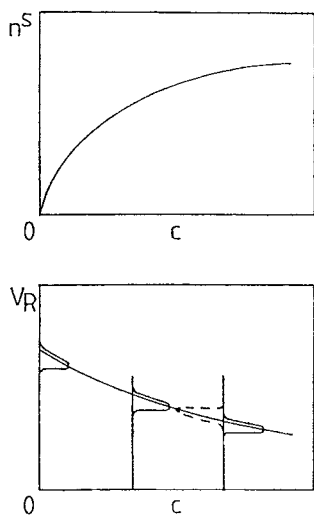


Figure 1. Shape and retention volume V_R of an elution peak in the case of a Langmuir-type isotherm.

isotherm regions at low concentrations.^{7,8} The present paper is focused on low adsorbed amounts of the poorly detectable surfactant octa(oxyethylene) monododecyl ether ($C_{12}E_8$). Hence, the corresponding concentration range is investigated in detail. Furthermore, measurements at various temperatures are performed, since the influence of temperature on the adsorption allows insights into the adsorption mechanism.

Background

“Elution on a Plateau” Method. In chromatographic elution analysis, the shape and the retention volume of a peak are connected with the form of the isotherm.¹⁷ In the following, only “concentration peaks” are considered; i.e., the injected sample consists of the same components as the eluent and differs from the eluent only in concentration. In the ideal case, the sample disturbs the eluent concentration only infinitesimally. The retention volume V_R , which is the product of the retention time and the flow rate, of an injected disturbance corresponds to the derivative of the isotherm at the eluent concentration c (see below). In the case of L(angmuir)-type isotherms, peaks have tails. Thus the retention volume of a peak decreases with increasing eluent equilibrium concentration, as Figure 1 shows. In contrast, in the initial region of an S-shaped isotherm, the retention volume increases with the concentration. Analyses at different eluent concentrations and integration of the measured retention volumes give the adsorption isotherm, which shows the sorbed amount n^S as a function of the equilibrium concentration.

These facts are used by the so-called “elution on a plateau” (EP) method, which till now has been mainly applied in gas chromatography.^{16,18} This method, also known as the “step and pulse”¹⁹ or “minor disturbance” technique,²⁰ has more recently been transferred to liquid chromatography.²¹

The relationship between adsorption and retention in liquid–solid chromatography can be described by the model of the idealized chromatographic column.²² For

elution analysis under isocratic and isothermal conditions, it is assumed that the column is equilibrated with an eluent of concentration c^l before injection and that the injected sample i is infinitesimal. The volume of the liquid phase in the column, which will be designated as the dead or, rather, holdup volume, is subtracted from the measured retention volume. The difference is called the net retention volume, which is related to the sorbed amount, specifically the surface excess on the volume basis $n_i^{\sigma(v)}$.^{23,24} For a concentration pulse of the EP method, the system can be simplified and the corresponding net retention volume $V_{N,i}$ can be expressed by

$$V_{N,i} = \partial n_i^{\sigma(v)} / \partial c_i^l \quad (1)$$

This means the slope of an isotherm is equivalent to the net retention volume. The determination of an isotherm requires measurements at different eluent concentrations. Integration up to the eluent concentration c_i^l amounts to the corresponding surface excess:

$$n_i^{\sigma(v)} = \int_0^{c_i^l} V_{N,i}(c_i^l) dc_i^l \quad (2)$$

The surface excess concentration is obtained through division by the surface area.

With the EP method, the investigation of both adsorption and desorption isotherms is possible. For desorption measurements, the concentration of the component of interest is lower in the injection than in the eluent. The so-called negative pulse obtained is related to a point on the desorption isotherm.

The Zhu and Gu Adsorption Isotherm. For the adsorption of surfactants at solid–liquid interfaces, Zhu and Gu suggested a general isotherm model on the basis of a two-step adsorption mechanism and mass-action treatment.¹³ The model assumes the formation of surface aggregates or hemimicelles. The proposed general isotherm equation is

$$n_i^{\sigma(v)} = \frac{n_{\max} K_1 c_0 (1/n + K_2 (c/c_0)^{n-1})}{1 + K_1 c_0 (1 + K_2 (c/c_0)^{n-1})} \quad (3)$$

where n_{\max} is the maximal surface excess at high concentrations, K_1 and K_2 are the equilibrium constants involved in the adsorption of monomers onto the first layer and the formation of hemimicelles, respectively, c_0 is 1 mol m^{-3} , and n is the aggregation number of hemimicelles. For $K_2 \rightarrow 0$ and $n \rightarrow 1$, the equation reduces to the Langmuir equation. Equation 3 was successfully used to evaluate LS- and S-type adsorption isotherms of surfactants on solids.²⁵ In analogy to micellization, above the hemimicelle concentration (hmc), which refers to hemimicelles formed on the surface, the adsorption increases dramatically. For LS-type isotherms, the hmc can be calculated according to

$$\text{hmc} = c_0 ((n-2)/n)^{n/(n-1)} K_2^{1/(1-n)} \quad (4)$$

Thermodynamics. From adsorption isotherms and their temperature dependence, thermodynamic data can be calculated. In the following, only diluted binary solutions are considered, i.e., the mutual displacement of the two components at the interface. The Gibbs free energy

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of displacement $\Delta_{21}G$ according to the general Gibbs adsorption isotherm²⁶ is

$$\Delta_{21}G = -RT \int_0^{\Gamma_2} \frac{d\Gamma_2}{c_2} \quad (5)$$

and the enthalpy of displacement $\Delta_{21}H$ according to the Clausius–Clapeyron equation for constant surface excess²⁷ is

$$\Delta_{21}H = -RT^2 \frac{\partial \ln c_2}{\partial T} \quad (6)$$

Experimental Section

Materials. As the nonionic surfactant, monodispersed octakis-(oxyethylene) monododecyl ether ($C_{12}E_8$) from Fluka with a purity >98% was chosen. Its cloud point is approximately 350 K, and its critical micelle concentration (cmc) at 298 K is 0.08 mol m^{-3} .²⁸ For batch measurements, a radioactively labeled surfactant was used. Inactive $C_{12}E_8$ was labeled by catalytic tritium exchange at the Zentralinstitut für Kernforschung, Rossendorf, Germany. The resulting specific activity was 150 TBq mol^{-1} . Unmodified silica gel LiChrospher Si 1000-10 from Merck was used as the adsorbent. This macroporous material consists of spherical particles of $10 \mu\text{m}$ diameter and contains pores with a diameters of about $0.1 \mu\text{m}$. LiChrospher Si 1000-10 has a specific surface area of $30 \text{ m}^2 \text{ g}^{-1}$. The water used was triply distilled and filtered through a $0.2 \mu\text{m}$ filter of cellulose nitrate.

Chromatographic Methods. A conventional HPLC unit was used for the isocratic runs. An aqueous surfactant solution as the mobile phase or eluent entered an SP 8810 pump (Spectra Physics) via a Degasys DG-1200 vacuum degasser (Uniflows). Approximately 1 g of the silica gel was contained in an HPLC column ($150 \times 4.6 \text{ mm}$). Since the adsorbent was slightly soluble in the eluent, a precolumn with the same adsorbent and dimensions was installed to saturate the eluent. For protection, the column packages were stored under methanol. A 7125 injector (Rheodyne) with a sample loop of 20 mm^3 was installed between the two columns. The columns and the injector were accommodated in a column thermostat (W. O. Electronics), and the column outlet was connected to a thermostated RI SE-61 differential refractometer (Shodex), a universal detector.

The measurements were carried out at column temperatures of 278, 298, and 318 K. The normal flow rate was $16.7 \text{ mm}^3 \text{ s}^{-1}$. In the case of extreme retention volumes, it was changed to 6.7 or $41.7 \text{ mm}^3 \text{ s}^{-1}$. For sufficient accuracy, the flow rates were controlled gravimetrically. Unretarded tracers are ideal for estimating holdup volumes. Isotopically substituted analogues of eluents meet this requirement best,²⁹ so deuterated water was applied.

The expansion of an eluent due to the pressure drop across a column and to the temperature difference between the column and its outlet leads to systematic errors in the flow rate. Therefore, it was necessary to correct the retention volumes V .³⁰ The pump internally compensates for the compressibility of common organic solvents. Since the isothermal compressibility α of diluted aqueous solutions and water is lower, the pump overcompensates for the compression. The mean column pressure is approximated as a quarter of the pump pressure p , since the precolumn has the same dimensions as the main column. For the correction of the thermal contraction or expansion between the column temperature T_C and outlet temperature T_E , the thermal expansion coefficient α of water is used:

$$V_{\text{corr}} = V \exp(\alpha(T_C - T_E) + ((\text{const} - \alpha) - \alpha/4)p) \quad (7)$$

Adsorption excess amounts were also determined by the frontal

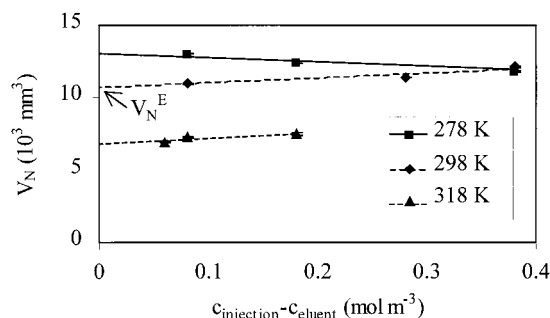


Figure 2. Net retention volumes V_N as functions of the injection concentration minus the eluent concentration of 0.02 mol m^{-3} $C_{12}E_8$ at various temperatures.

analysis method.³¹ Technical details of the employed setup, method, and evaluation are given elsewhere.³²

Batch Method. The radioactively labeled surfactant was diluted with inactive material.³³ The surfactant solution was added to the suspended silica gel in water, and the specimen was shaken. Following ultracentrifugation, the activity of the supernatant solution was measured by a scintillation counter after the addition of a liquid scintillation cocktail. From the activity, the equilibrium concentration c_i was calculated. The volume-reduced surface excess concentration $\Gamma_i^{(v)}$ was obtained by

$$\Gamma_i^{(v)} = (c_{i,0} - c_i) V / m a_s \quad (8)$$

where $c_{i,0}$ is the initial concentration, V the volume of the liquid phase, m the mass, and a_s the specific surface area of the adsorbent, respectively.

Results

To investigate adsorption isotherms of the nonionic surfactant octa(oxyethylene) monododecyl ether ($C_{12}E_8$) on silica gel, the “elution on a plateau” (EP) method, described above, was used. Aqueous $C_{12}E_8$ solutions served as the eluent and as the injected samples with concentrations which deviated from that of the eluent. As known from chromatography, the retention of a sample depends on its injected amount. The frequent neglect of this fact leads to systematically incorrect results. Since infinitesimal disturbances would be ideal but not detectable, for correct results the retention volumes of the dilution series were measured and extrapolated here. In general, the dilution series consisted of three or more concentrations. Each solution was injected a minimum of three times, and the mean retention volume was calculated. Subtracting the holdup volume gave the net retention volume V_N , which was plotted as a function of the injection concentration c_{inject} minus the eluent concentration c_{eluent} for evaluation. Figure 2 shows an example of such plots for a certain eluent concentration at various temperatures. In such plots, linear increases or decreases in the retention volumes are frequently observed. The net retention volume of an infinitesimal disturbance is accessible by linear extrapolation to zero concentration.

To determine a sorption isotherm, measurements at different eluent concentrations were performed. Starting with pure water, the eluent concentration of $C_{12}E_8$ was increased in small steps. Figure 3 displays the extrapolated net retention volumes V_N^E as functions of the eluent concentration c at 278, 298, and 318 K.

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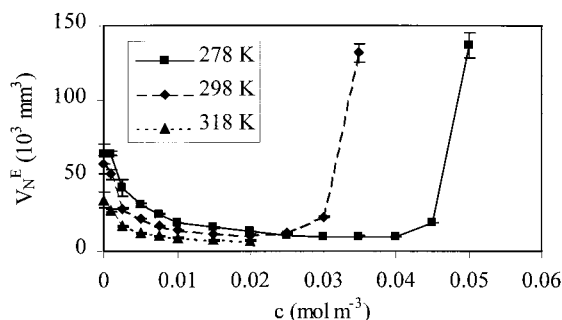


Figure 3. Extrapolated net retention volumes V_N^E as functions of the eluent concentration c of $C_{12}E_8$.

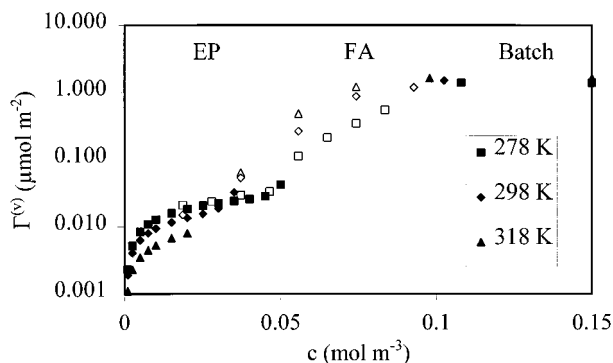


Figure 4. Isotherms for the adsorption of $C_{12}E_8$ from water onto the silica gel LiChrospher 1000-10 at various temperatures: elution on a plateau (EP) and batch methods, filled symbols; frontal analysis (FA), open symbols.

There is a maximum of the net retention volume at zero surfactant concentration for each temperature. With increasing surfactant concentrations, the retention volumes decrease. At concentrations of 0.035 and 0.05 mol m^{-3} , there are additional maxima of the net retention volumes for 298 and 278 K, respectively. Large net retention volumes as in the present case are problematic because their determination is uncertain due to the long retention times and the great disturbances required. Therefore, in the examined system the second maximum, which corresponds to a steep isotherm step, could not be estimated in detail. Hence, the surface excesses in this range were determined by frontal analysis. Furthermore, the surface excesses at concentrations above this isotherm step were measured by the batch technique. Figure 4 shows the surface excess concentration Γ on a logarithmic scale as a function of the concentration at the three temperatures. The surface excess results partially from the integration of the net retention volumes in Figure 3 according to eq 2.

Isotherms of the two-step type are found for the adsorption of the poly(oxyethylene) monoalkyl ether from water onto the silica gel at all temperatures investigated. The adsorbed amount of the lower first plateau decreases with increasing temperature. In contrast, at the second plateau, which is 2 orders of magnitude higher than the first plateau, the surface excess concentration increases from 1.4 $\mu\text{mol m}^{-2}$ at 278 K through 1.5 $\mu\text{mol m}^{-2}$ at 298 K up to 1.65 $\mu\text{mol m}^{-2}$ at 318 K. Therefore, the step height between the two plateaus grows with temperature. Furthermore, the beginning of this step is shifted to lower concentrations with increasing temperature.

Discussion

Two-step isotherms are found for the adsorption of monodispersed octa(oxyethylene) monododecyl ether

($C_{12}E_8$) from water on the hydrophilic macroporous silica gel LiChrospher Si 1000-10 at 278, 298, and 318 K. They are L4-type isotherms according to Giles et al.³⁴ For the adsorption of poly(oxyethylene) monoethers from water onto silica (Triton, $C_{12}E_6$, $C_{12}E_8$,¹⁰ C_8E_4 ⁶ onto macroporous silica; $C_{12}E_6$ and $C_{12}E_{25}$ onto silica nanoparticles⁵), often only S2-type isotherms are found, whereas there are only a few examples of L4-type isotherms, i.e., a Langmuir-type isotherm region at low concentrations (C_8E_4 adsorbed onto controlled-pore glass;⁷ poly(oxyethylene) monoalkyl ethers adsorbed onto silica nanoparticles⁸). Therefore, a focus of the present study is adsorption at low concentrations to obtain more information concerning rarely investigated adsorption processes in this range. In all systems, the surface excess concentration at low equilibrium concentration was more than 1 order of magnitude lower than the maximal one. The maximal surface excess concentrations in the present work are near 3.1 $\mu\text{mol m}^{-2}$ at 293 K and 3.6 $\mu\text{mol m}^{-2}$ at 318 K for a closely related system.¹⁰ At the second plateaus in Figure 4, only two-thirds of the 1.7 nm^2 maximal molecular area of the surfactant is available. The contribution of the dodecyl group is 0.7 nm^2 calculated from van der Waals radii. As poly(oxyethylene) chains are randomly coiled in water, their area was calculated by multiplying the square root of the number of oxyethylene units in a chain with a constant taken from ref 35. The area of the octa(oxyethylene) group is at most 1 nm^2 , and its cross section amounts to 0.5 nm^2 . Furthermore, it was found that pure poly(ethylene oxide) adsorbs onto silica gel.⁵ Thus, the nonionic surfactant can adsorb onto the hydrophilic silica gel predominantly over the hydrophilic oxyethylene groups through hydrogen bonding. For the poly(oxyethylene) chains alone, the surface area of the silica gel is sufficient. The surface excess concentration of the second plateau increases slightly with temperature, in accordance with the literature.^{6,10} This can be explained by the decreasing hydration of the oxyethylene groups, which allows closer packing of surfactant molecules.³⁶ In contrast, at the first plateau, the surface excess concentration sinks with increasing temperature, which is explained below. Since this surface excess concentration is much lower than that of the second plateau, the surfactant molecules can lie singly and flat on the surface of the silica. The same temperature behavior of the two plateaus was observed for the adsorption of the smaller homologue C_8E_4 onto silica.⁶

The second isotherm steps in Figure 4 (log-normal) are relatively steep. For the adsorption onto silica gel of monodispersed poly(oxyethylene) monododecyl ethers with a degree of ethoxylation below 10, sudden increases in the adsorption up to a plateau were also reported.^{5,8,10} It should be noted that, for polydisperse or longer poly(oxyethylene) monoethers, the steps were less steep. In the adsorption plateau, fragmented bilayers of adsorbed surfactant molecules were indicated by neutron reflection measurements.⁵ On the other hand, atomic force microscopy showed globular structures of $C_{12}E_8$ on silica similar to micelles.¹² The center-to-center separation of the globular structures corresponded to the length of two surfactant molecules. Therefore, it was suggested that these globular structures are hemimicelles. These are small surfactant aggregates held together by a hydrophobic effect. The formation of these structures on surfaces below the plateau

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Table 1. Parameters of the Isotherm Equation of Zhu and Gu for the Adsorption of C₁₂E₈ from Water onto Silica Gel at Various Temperatures

| <i>T</i> , K | <i>K</i> ₁ | <i>K</i> ₂ | <i>n</i> | hmc, mol m ⁻³ |
|--------------|-----------------------|-----------------------|----------|--------------------------|
| 278 | 11 | 2 × 10 ¹³ | 13 | 0.065 |
| 298 | 10 | 3 × 10 ¹⁵ | 14 | 0.050 |
| 318 | 6 | 7 × 10 ¹⁹ | 17 | 0.047 |

was proposed many years ago.^{37,38} This so-called hemimicellization is also assumed by the general isotherm model of Zhu and Gu. Their equation (i.e., eq 3) was used for the evaluation of the two-step isotherms obtained in the present work. It was solved iteratively by minimizing the sum of least squares between the calculated and the measured surface excess concentrations. The critical hemimicelle concentration (hmc) was calculated according to eq 4. Table 1 lists the values for the two equilibrium constants *K*₁ and *K*₂, the aggregation numbers of hemimicelles *n*, and the hmc's at 278, 298, and 318 K.

The hmc's are located at the beginning of the S-shape range of the isotherms according to the model. The critical micelle concentration (cmc) of the C₁₂E₈ used amounts to 0.08 mol m⁻³ at 298 K. It is slightly above the step. For comparable systems, it was found that the cmc is at the beginning of the second plateau.^{5,7} With rising temperature, the beginning of the second step and thus the hmc are shifted to lower concentrations. The same shift of the step with the temperature was observed for the C₈E₄ system.⁶ The cmc of poly(oxyethylene) monoalkyl ethers such as the surfactant used sinks with increasing temperature, also.³⁹ The reason for these shifts is the increasing dehydration of the hydrophilic group with temperature. Thus the hydrophobicity of the surfactant molecules and their aggregation tendency increases with the temperature. The hydrophobicity of the surfactant also increases with salt addition, an increase in the alkyl chain length, or with a decrease in the number of oxyethylene units. Indeed, investigations of these parameters for surfactant adsorption showed a shift of the sharp step to lower concentrations and an increase of the plateau value with increasing hydrophobicity.^{10,11}

The aggregation number of hemimicelles *n* in Table 1 corresponds to the ratio between the first and second plateau in Figure 4. The number at 298 K is lower than the corresponding aggregation number⁴⁰ of approximately 100 for C₁₂E₈ micelles in water, in agreement with the fact that hemimicelles are only partial micelles. Using the same approach for C₈E₄, aggregation numbers of the hemimicelles⁶ were found below or near those of the micelles.⁴¹ For C₈E₂₅, the aggregation number in the adsorbed layer at the cmc calculated by the self-consistent-field lattice theory was the same as that for the micelles.⁵ Because of the opposite temperature dependences of the first and second plateaus, the step height and thus the aggregation number of hemimicelles, as well as the equilibrium constant *K*₂, which is involved in the formation of hemimicelles, increase with temperature. The aggregation number of micelles of poly(oxyethylene) monoalkyl ethers presents the same temperature behavior.³⁹ Both can be explained by the increasing dehydration of the

oxyethylene groups with temperature, which results in a decreasing volume of the hydrophilic group.

For low concentrations of the adsorption isotherms at the three temperatures, thermodynamic data were calculated. Equation 5, which gives the Gibbs free energy of displacement, yielded negative free energies. Like the surface excess, the absolute value of the free energy decreases with increasing temperature. From inspection of the isotherms, e.g., at 278 and 298 K in Figure 4, an enthalpy of displacement can be estimated according to eq 6. The enthalpy is exothermic at low concentrations and endothermic above the crossing of the two isotherms, the beginning of the steep increase. Calorimetric studies of related systems confirm this.^{6,7} The exothermic heat effect at low surface coverage can be explained by the adsorption of individual surfactant molecules through hydrogen bonds between oxyethylene groups and surface silanol groups. Hydrogen bonds are weakened with increasing temperature;¹¹ thus the surface excess decreases as found. This is supported by the pronounced Langmuir shape of the isotherms found at these low concentrations. In the second isotherm step, the adsorption is endothermic; thus this adsorption must be entropy driven. The entropy gain can come from the formation of surface aggregates through hydrophobic interactions between the alkyl chains. Therefore, the hydrogen-bonded water clusters around the hydrophobic alkyl chains of the monomers must be broken endothermically. All the results above reflect an analogy between the nature of hemimicellization and that of micellization.

For the measurement of sorption isotherms, frontal analysis (FA) was recently used.^{6,7} This is a chromatographic method like the EP technique. Both methods differ in the quantities of the samples injected. FA switches between solutions of different concentrations, whereas in EP only a small concentration pulse is injected. Additionally, in EP the equilibrium concentration is given, while in FA it is the average of the two concentrations that is given. Furthermore, in FA the detector limits the minimum concentration difference, which can be evaluated. Therefore, disadvantages of the FA technique are that a second pump is often required to deliver larger volumes of the second solution and investigations at low concentrations are barely possible due to the detection limit. On the other hand, in FA the return to the initial concentration is linked with the desorption isotherm. The chromatographic techniques as dynamic methods can also simulate the transport behavior of the compound used in the column material. Whereas FA resembles the continuous addition of substances, such as in technical processes, the EP technique corresponds to point sources, such as the entry of chemicals into the soil by an accident or pesticide application. The results of the presented work can be interpreted as follows. When, e.g., a solution of a poly(oxyethylene) monoether enters a soil that consists of silica compounds, the nonionic surfactant can be transported by rainwater through the soil into the groundwater. The retention or delay time of the surfactant in the soil will increase with decreasing temperature, as Figure 3 shows. Furthermore, the delay time of the surfactant will decrease with an increasing amount of added surfactant (compare Figures 1 and 2). In general, the danger potential of chemical compounds for environmental compartments can be estimated and taken into account, e.g., for decontamination.

A common method for the determination of sorption isotherms is the batch technique. In comparison with the batch technique, chromatographic methods have several advantages: The measuring system can be thermostated

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easily and completely. Since the system is nearly closed, it is suitable for volatile and/or hazardous compounds. In addition, the accuracy of the surface excess value, which is measured more directly, is often better. The investigation of poorly detectable substances, at low concentrations and/or at low surface excess, is also possible. This is especially important from the standpoint of environmental concerns. Desorption isotherms, like adsorption isotherms, can easily be determined using injections with concentrations below the eluent concentration. As mentioned above, the transport behavior can be investigated, which is of technical as well as environmental interest. From the isotherm derivative measured, more details of the isotherm can be obtained. An advantage of the EP technique is that the equilibrium concentration is given. On the other hand, the investigation of steep isotherm regions is problematic because of the corresponding large net retention volumes, as mentioned.

Conclusions

A liquid chromatographic method for the determination of sorption isotherms is presented. The so-called "elution on a plateau" technique measures the derivatives of sorption isotherms. With this elution analysis, the adsorption of a nonionic surfactant from water onto a macroporous silica gel is investigated at various temperatures. Two-step isotherms are found. The surface excess of the first step, which up to now has rarely been observed,

is 2 orders of magnitude lower than that of the second plateau. At these low concentrations, the isotherm exhibits a pronounced Langmuir shape and the surface excess decreases with increasing temperature. The isotherms can be described well by the general equation of Zhu and Gu, which assumes the formation of hemimicelles at the surface. A comparison of the temperature behaviors of the formations of hemimicelles and micelles yields many agreements.

In comparison with the common batch technique, chromatographic methods have some advantages for the determination of sorption isotherms. With the nearly closed measuring system, complete temperature control can easily be realized and volatile or hazardous compounds can be handled safely. Furthermore, chromatographic methods allow the relatively simple measurement of desorption isotherms, as they do in the case of adsorption isotherms. Additionally, with chromatographic methods as dynamic techniques, the transport behaviors of investigated substances can be examined. Overall, chromatographic methods are valuable tools for the determination of sorption isotherms.

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